CHEMISTRY OF ETHYLENEIMINE

III. Reaction of N-Aminoethyleneimine with the Simplest Aliphatic Aldehydes and Acrolein*

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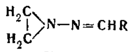
The mechanism of the reaction of N-aminoethyleneimine with some aliphatic aldehydes and with acrolein have been studied. It has been shown that the reaction takes place at the carbonyl bond C=O with the formation of hydrazones.

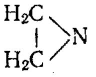
Two of us previously showed that in the reaction of ethyleneimine with aliphatic aldehydes the true reaction products are diaziridinomethane derivatives and not hydroxymethylethyleneimines [2–4].

The present work was devoted to a study of the reaction of aliphatic aldehydes with N-aminoethyleneimine (I), the molecule of which, while preserving the main properties of the simplest nitrogen-containing heterocycle, acquires a number of interesting new properties characteristic for an amino group conjugated with the heterocycle as a whole [5].

Of course, the reaction of aldehydes with I will take place differently from that with ethyleneimine [2, 3], since I can be regarded as an analog of an unsymmetrically-substituted hydrazine. In actual fact, in this case the main reaction products are the hydrazones II–IV.


II–IV

II $R = CH_3$; III $R = C_2H_5$; IV $R = C_3H_7$

The structure of II–IV was shown by elementary analyses and PMR spectra. The IR spectra of these compounds contain characteristic frequencies of the HC=N group (1650 cm^{-1}) and of the  group (3010, 3080 cm^{-1}).

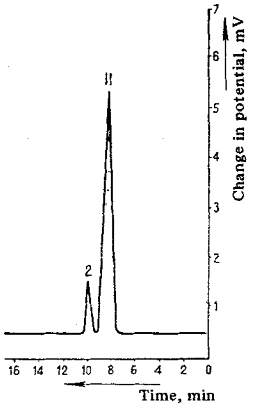


Fig. 1. Chromatogram of the products of the transformation of ethylideneaminoethyleneimine: II) ethylideneaminoethyleneimine; 2) acetaldehyde azine.

Compounds II–IV are colorless liquids readily soluble in ether, ethanol, and water, possessing the characteristic odor of the corresponding aldehydes. Compounds II–IV are more stable than I, but on storage they undergo certain changes, the main indication of which is the appearance of a yellow-green coloration. By means of gas-liquid chro-

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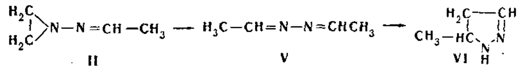
*For part II, see [1].

matography we have succeeded in showing that this change leads to the formation of a new compound. Thus, in particular, for II a peak appears (Fig. 1) which characterizes the presence of fraction 2 in the mixture. The latter was isolated by preparative gas-liquid chromatography. The IR spectrum of fraction 2 exhibits a strong absorption band at 1645–1650 cm^{-1} which is characteristic for a C=N bond, and also characteristic frequencies at 1445–1475, 1220, 1270, 1275, and 975–920 cm^{-1}. The latter apparently are due to the formation vibrations of a CH_3 group and to the planar and nonplanar vibrations of a CH=N group. At the same time, the results of elementary analysis and a determination of the molecular weight of the "impurity" component 2 show that the latter is an isomer of compound II. This makes is possible to assume that II isomerizes into acetaldehyde azine (V) with a possible conversion into 5-methylpyrazoline (VI) [6].



The isomerization of II into V is apparently facilitated by the presence of the peculiarly hybridized nitrogen atom (sp^{2,3}) in the ethyleneimine ring, which explains the partially azine nature of II. The establishment of the true structure of the substance of fraction 2, i.e., to make a choice between the proposed structures V and VI, is possible by means of the PMR spectrum. The latter contains a CH_3 doublet (8.18 ppm) and a CH quartet (2.26 ppm) with J_{H-H} = 5.3 Hz, which is characteristic for the $CH_3CH{=}N$ fragment present only in the structure V. Thus, structure VI is excluded for this substance. The complete agreement of the physical and spectral characteristics of the acetaldehyde azine obtained by independent synthesis from acetaldehyde and hydrazine with the substance of fraction 2 conclusively showed the structure of V.

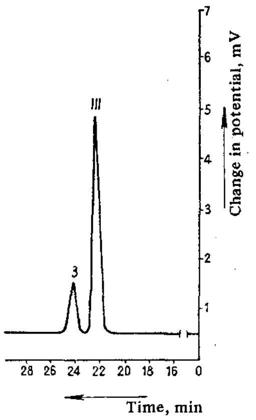
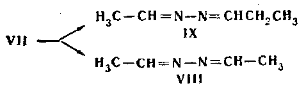


Fig. 2. Chromatogram of the product of the transformation of propylideneaminoethyleneimine: III) propylideneaminoethyleneimine; 3) propionaldehyde azine.

We have observed a similar isomerization in the homologs of II; thus, for example it was found that, on storage, III is converted into the mixed (unsymmetrical) acetaldehyde-propionaldehyde azine (ethylidenehydrazonopropane) (VII):

$$\text{III} \longrightarrow \underset{\text{VII}}{H_3C{-}CH{=}N{-}N{=}CHCH_2CH_3}$$

The isomerization product can be isolated from the mixture formed on the storage of III by means of preparative gas chromatography (Fig. 2). The determination of the structure of this substance is complicated by the fact that, according to the investigations of B. V. Ioffe, A. P. Kochetkov, et al., mixed azines readily undergo disproportionation to form a mixture of the symmetrical azines and, conversely, under certain conditions an equimolecular mixture of symmetrical azines forms the corresponding unsymmetrical azines [7].



$$\text{VII} \longrightarrow \begin{cases} \underset{\text{IX}}{H_3C{-}CH{=}N{-}N{=}CHCH_2CH_3} \\ \underset{\text{VIII}}{H_3C{-}CH{=}N{-}N{=}CH{-}CH_3} \end{cases}$$

Thus, as can easily be seen, it is impossible to use only the results of elementary analysis, IR spectra, and PMR spectra to establish the presence in the system of VII or, as the case may be, VIII and IX. The presence of only one peak in the chromatogram given by fraction 3 does not show the presence of only one product since, according to the literature, a mixture of symmetrical azines is converted into the mixed azine in the vapor phase at a temperature of 40° C [7]. Consequently, to detect VII, VIII, and IX in fraction 3 we had recourse to developmental chromatography on alumina [7], since the values for the product VII obtained by a different method and also for VIII and IX have been determined. The chromatography of fraction 3 carried out under similar conditions gave R_f 0.53. The almost complete agreement of this figure with that for VII (R_f 0.55) permitted the conclusion that the substance of which fraction 3 consisted possessed the structure VII.

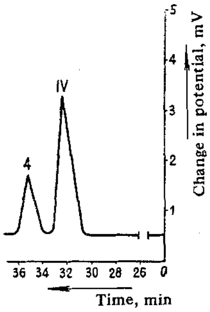
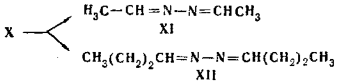


Fig. 3. Chromatogram of the products of the transformation of butylideneaminoethyleneimine: IV) butylideneaminoethyleneimine; 4) butyraldehyde azine.

Compound IV isomerizes similarly. The isolation of fraction 4 (Fig. 3) from the mixture in the pure state by means of preparative gas-liquid chromatography presented no problems. According to the results of elementary analysis and a molecular-weight determination, the composition of the substance in the fraction corresponded to X.

$$\mathrm{IV} \longrightarrow \underset{\mathrm{X}}{\mathrm{H_3C{-}CH{=}N{-}N{=}CHCH_2CH_2CH_3}}$$

As in the preceding cases, the IR spectrum of fraction 4 showed characteristic frequencies for the HC=N groups (1650 cm^{-1}), CH_3 groups (1475 cm^{-1}), and CH_2 groups (1460 cm^{-1}).

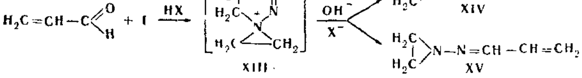


$$\mathrm{X} \begin{cases} \nearrow \underset{\mathrm{XI}}{\mathrm{H_3C{-}CH{=}N{-}N{=}CHCH_3}} \\ \searrow \underset{\mathrm{XII}}{\mathrm{CH_3(CH_2)_2CH{=}N{-}N{=}CH(CH_2)_2CH_3}} \end{cases}$$

Compound X has not been described in the literature and its R_f value is not given, but from a comparison with XII [7] it must be assumed that the substance of fraction 4 is not a mixture of XI and XII but is X.

The developmental chromatography of this fraction confirmed the presence of a single product and the absence of an equimolecular mixture. We have also investigated the structure of the product of the reaction of I with the simplest unsaturated aldehyde, acrolein. In agreement with information in the literature, the reaction of acrolein with salts of unsymmetrical dimethyl- and diethylhydrazines forms quaternary-pyrazolinium salts which undergo the amino-nitrile rearrangement under the action of alkali in the cold [8–12].

By means of gas-liquid chromatography, we isolated from the mixture of products from the reaction of I with acrolein, which polymerized fairly rapidly, an individual substance the yield of which was only 20–25%, calculated on the I (Fig. 4). The IR spectrum of the substance isolated contained absorption bands at 1670 and 1570 cm^{-1} characteristic for the >C=CH—C=N conjugated system while there were no bands in the 2245–2247 cm^{-1} region characteristic for the nitrile group and there were bands corresponding to an ethyleneimine ring at 3010, 3080, 1220, and 824 cm^{-1}. This indicates that the product of the reaction of I with acrolein is not β-ethyleneiminopropionitrile (XIV), the formation of which could have been expected by analogy with previous work [8–12], but N-allylidene-N',N'-ethylenehydrazine (XV).



This can apparently be explained by the assumption that the pyrazolinium salt of ethyleneimine, in contrast to the pyrazolinium structures of the unsymmetrical dialkylhydrazines, cannot, because of the low stability of the iminium ion of ethyleneimine, change into compound XIV since if structure XIII were formed at all, polymerization should take place preferentially with the opening of the ethyleneimine ring to form various condensation products. The main product is XV.

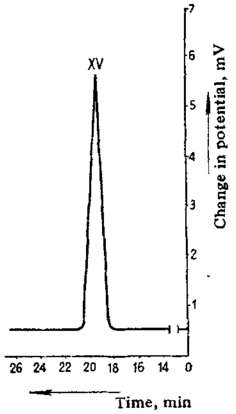


Fig. 4. Chromatogram of the product of the reaction of N-aminoethyleneimine with acrolein: XV) allylideneaminoethyleneimine.

The presence of a conjugated bond for the unsaturated hydrazone in the system is also confirmed by the high value of the molecular exaltation calculated from the appropriate values of the molar refraction for XV.

EXPERIMENTAL

Ethylideneaminoethyleneimine (II). With stirring and cooling to 0° C, 4.4 g (0.1 mole) of acetaldehyde was added to 5.8 g (0.1 mole) of I in 25 ml of ether. The reaction was accompanied by a considerable spontaneous rise in temperature. After the completion of the addition of the aldehyde, the mixture was kept at room temperature for 2 hr and was dried with sodium sulfate. Its composition was determined by gas-liquid chromatography (see Fig. 1). The analysis was carried out on a "Tsvet-1" chromatograph using a thermal conductivity detector. Bp 87–88° C, d_4^{20} 0.8752, n_D^{20} 1.4412. Found, %: C 56.87; H 10.01; N 33.02; MR 25.65. Calculated for $C_4H_8N_2$, %: C 57.14; H 9.55; N 33.2; MR 25.084.

Propylideneaminoethyleneimine (III). This was obtained in a similar manner to II from I and propionaldehyde. Bp 118–120° C, d_4^{20} 0.8759, n_D^{20} 1.4430. Found, %: C 60.7; H 10.56; N 29.0; MR 30.32. Calculated for $C_5H_{10}N_2$, %: C 61.2; H 10.2; N 28.6; MR 29.759.

Butylideneaminoethyleneimine (IV). This was obtained in a similar manner to II from I and butyraldehyde. Bp 152–154° C, d_4^{20} 0.8764, n_D^{20} 1.4442. Found, %: C 64.0; H 11.0; N 24.47; MR 34.83. Calculated for $C_6H_{12}N_2$, %: C 64.3; H 10.7; N 25.0; MR 34.48.

N-Allylidene-N',N'-ethylenehydrazine (XV). With vigorous stirring and cooling to –10° C, freshly-distilled acrolein stabilized with hydroquinone was added dropwise to a solution of 5.8 g (0.1 mole) of I in 30 ml of absolute ethanol and 0.01 mole of butyric acid. After the end of the reaction, 10 ml of 40% aqueous KOH was added. The product was salted out by the addition of solid KOH. The organic layer was separated off in a separating funnel and dried with magnesium sulfate for a day. The composition of the reaction mixture was determined by means of a "Tsevt-1" gas chromatograph under conditions similar to those for the analysis of II–IV. The isolation of the XV was exactly the same as that of products II–IV. Bp 136–137° C, d_4^{20} 0.9512, n_D^{20} 1.5210. Found, %: C 60.01; H 9.11; N 30.05; MR 30.12. Calculated for $C_5H_8N_2$, %: C 60.5; H 8.76; N 29.72; MR 29.254.

Acetaldehyde azine (V). This was isolated in the pure state by preparative gas-liquid chromatography from a mixture with the product II. Bp 92–93° C, d_4^{20} 0.8356, n_D^{20} 1.4404. Found, %: C 56.92; H 10.61; N 33.0; MR 26.51. Calculated for $C_4H_8N_2$, %: C 57.14; H 9.55; N 33.2; MR 26.50.

Ethylidenehydrazonopropane (VII). This was isolated under similar conditions from a mixture with product III. Bp 126–128° C, d_4^{20} 0.8362, n_D^{20} 1.4456. Found, %: C 61.0; H 9.75; N 29.2; MR 31.90. Calculated for $C_5H_{10}N_2$, %:

C 61.2; H 10.2; N 29.6; MR 31.158.

Ethylidenehydrazonobutane (X). This was isolated under similar conditions from a mixture with product IV. Bp 159–162° C, d_4^{20} 0.8376, n_D^{20} 1.4482. Found, %: C 64.0; H 10.8; N 24.8; MR 34.82. Calculated for $C_6H_{12}N_2$, %: C 64.3; H 10.7; N 25.0; MR 34.90.

Method of isolating the compounds. The isolation of II, 2, III, 3, IV, 4, and XV from the reaction mixture was carried out on a PLK-3 preparative chromatograph using an automatic fraction collector. The stationary phase was 25% of E-301 on modified INZ-600, 0.5–0.25 mm fraction. The length of the column was 8 m and its diameter 18 mm. A flame ionization detector was used in a bypass with traps. The carrier gas was nitrogen. $V = 600\ cm^3/min$; temperature of the thermostat 80° C; temperature of the evaporator 120° C.

The identification of the substances isolated in the preparative chromatograph was carried out on a "Tsvet-1" chromatograph using a katharometer as detector. The stationary phases used were 25% of E-301, 10% of PEG-1200, and 15% of polyethyleneimine M-1200 on Celite-545; mixed columns were also used. Temperature of the thermostat 80° C; temperature of the evaporator 120° C; I = 250 mA; carrier gas helium, $V = 46.6\ cm^3/min$.

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